CHAPTER II
QUALITY ASSURANCE

SECTION A

INTRODUCTION

Title I, §117 of the Clean Water Act requires that the Chesapeake Bay Program Office (CBPO) support the Chesapeake Executive Council by implementing and coordinating science, research, modeling, support services, monitoring and data collection. The CBPO has maintained and supported a research-quality monitoring program for Chesapeake Bay tidal waters since the late 1980s when standardized sampling, analytical and data management procedures were developed and coordinated with the then Maryland Office of Environmental Programs and the Virginia State Water Control Board. In the 1990s, standardized River Input monitoring was initiated to measure the nutrient and sediment loadings from the of the watershed's nine largest rivers. Nontidal water quality monitoring was later expanded upstream into rivers and streams across the Bay watershed, with all six participating jurisdictions now using comparable protocols.

Each of these monitoring programs provides an uninterrupted record of high-quality data that is used to calculate status and trends of water quality constituents over time. Trend analyses in particular require very reproducible data that are collected at the lowest possible limits of detection. Changes in methods, laboratories, instruments, sampling sites, etc., may affect the results so changes are carefully evaluated and approved to preserve the reproducibility of the data records over time.

A QA program shall be developed and implemented within the participants' organization that is in accordance with the procedures and recommendations of this document. The purpose of this chapter is to establish the data quality objectives and quality assurance protocols for incorporation into the participants' QA programs, Quality Assurance Project Plans (QAPP) and/or Standard Operating Procedures (SOP).

Section B of this chapter provides a description of the monitoring program's quality management system, documentation and general QA requirements. Section C covers the data quality objectives for field and laboratory operations. Section D is an overview of field quality control practices – more detailed requirements for Tidal and Nontidal Sampling are specified in Chapters IV and V. Section E describes inter-laboratory comparison studies, performance testing and external audits. Guidance for conducting comparability studies is given in Section F. Appendix II-A provides outlines for developing a Quality Assurance Project Plan and a Laboratory Manual.

SECTION B

QUALITY MANAGEMENT

1. Quality Management Systems

1.1. Organizations receiving EPA funds for monitoring are required to establish and document a formal quality management system (QMS) to ensure the generation of reliable and defensible data. A QMS is comprised of the organizational structure, objectives, policies, principles, responsibilities, and steps for ensuring quality and accountability in its work processes, products and services. A QMS includes:

1.1.1. Field operations and support functions used to assure consistency and data integrity: training, procurement, information management, records, management reviews of operations and data quality, evaluation criteria and follow up response.

1.1.2. Protocols for identifying out-of-control sampling, field measurements, and analytical conditions; processes for implementing and documenting the necessary corrective actions; decision rules and mechanisms for communicating the outcome.

1.2. The Chesapeake Bay Program recommends that participating laboratories develop and maintain a quality system that is equivalent to the National Environmental Laboratory Accreditation Institute (TNI) standards; however, laboratory accreditation is not required.

1.3. Laboratory quality management systems should be fully documented in a Laboratory Quality Manual (QM).

2. Quality Management Plans

2.1. State agencies receiving EPA funds for monitoring are required to document their quality management system in a Quality Management Plan (QMP).

2.2. EPA must review and approve the QMP prior to the initiation of environmental data collection and/or compilation activities. The document must be prepared in accordance with *EPA QA/R-2: EPA Requirements for Quality Management Plans*, which is available at www.epa.gov/quality1/qa_docs.html.

2.3. The QMP must be approved internally by the state QA Manager and the organization's senior management, and then be submitted to the EPA Project Officer at least **45** days prior to the initiation of data collection or data compilation. The U.S. EPA Region 3 Quality Assurance Manager approves the QMP.

2.4. An approved QMP is valid for up to five years unless there is a major program reorganization that affects quality assurance functions and structures in the organization.

3. Quality Assurance Project Plans

3.1. The Chesapeake Bay Quality Assurance Program requires the development and implementation of a Quality Assurance Project Plan (QAPP) for each of its monitoring activities. The QAPP addresses specific activities to be performed and procedures to be used by the Participant.

3.2. The major goals of the QAPP are to: 1) ensure that the level of needed data quality will be determined and stated before the data collection efforts begin and 2) ensure that all monitoring data generated and processed will reflect the quality and integrity established by the QAPP.

3.3. The QAPP is composed of standard elements that cover the entire project from planning, through implementation, to assessment. The document *EPA Requirements for QA Project Plans (QA/R-5)* fully describes the necessary elements which are outlined in Section F of this chapter.

3.4. Review and Approval of QAPPs

3.4.1 The EPA CBPO Project Officer and QA Coordinator will review and approve the QAPP at least to the "Conditional Approval Recommended" level (all technical issues having been resolved to the satisfaction of the CBPO) prior to data collection. The QAPPs shall be reviewed and approved in the context of the Program's DQOs.

3.4.2 The CBP QA Coordinator shall review and evaluate the implementation of the plans during the operational phases of sampling and analyses. The CBP QA Coordinator shall also assess the actual performance of the planned activity and subsequent results according to the criteria described in the QAPPs.

4. Laboratory Quality System and Manual

4.1. The purpose of the laboratory quality management system is to:

4.1.1. Maintain data integrity, validity, and usability.
4.1.2. Ensure that sampling and analytical systems are maintained in an acceptable state of stability and reproducibility.
4.1.3. Detect problems through data assessment and establish corrective action procedures to ensure that the sampling, analytical, and measurement processes are reliable.
4.1.4. Document all aspects of the sampling, analytical, and measurement processes in order to provide data that are technically sound and legally defensible.

4.2. The laboratory quality management system is to be documented in a Laboratory Quality Manual (QM). All policies and procedures governing the laboratory's quality system shall be documented in the QM. All laboratory personnel shall follow the policies and procedures established by the quality manual

4.3. The QM should present, in specific terms, the policies, organization, objectives, and specific QA and QC activities designed to achieve the data quality requirements recommended in this document. Where applicable, Standard Operating Procedures pertaining to each element should be included or referenced as part of the QM. The QM should be available during on-site laboratory evaluations.

4.4. Appendix II-A of this chapter includes an outline of key elements of the laboratory quality manual.

5. Standard Operating Procedures

5.1. A SOP is a written document which provides directions for the step-by-step execution of an operation, test, or action which is commonly accepted as the method for performing certain routine or repetitive tasks. These tasks include such operations as sampling, sample tracking, analysis, glassware preparation, instrument calibrations, preventive and corrective maintenance, and data reduction and analysis. SOPs should be expressed in terms of fixed protocols which must be followed. Where options exist, these should be clearly described, and criteria for the selection of alternatives must be included. SOPs should be written such that the actual practices are recorded.

5.2. SOPs should be clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts. All SOPs should reflect activities as they are currently performed in the field and laboratory. In addition, all SOPs should be:

5.2.1. Consistent with the field and laboratory methods contained in this document and/or or established by Chesapeake Bay Program Workgroups.

5.2.2. Consistent with applicable federal and state regulations and guidelines.

5.2.3. Adequate to establish traceability of standards, instrumentation, samples, and monitoring data.

5.2.4. Simple, so that any user with appropriate general education, experience, and training can duplicate the task as historically performed.

5.2.5. Consistent with a) sound scientific and engineering principles, b) instrument manufacturers' instruction manuals and c) good laboratory practices.

5.2.6. Complete enough so the user or auditor follows the directions in a logical step-wise manner through the sampling, analysis, and data handling processes.

5.3. Benefits of SOPs

5.3.1. Adherence to SOPs minimizes measurement bias and increases reliability.

5.3.2. Provide a record of the performance of all tasks at any fixed point in time.

5.3.3. Increase the opportunity for thorough review of procedures with appropriate sign-off by management.

5.3.4. Serve as a training document for new employees providing consistent performance of tasks.

5.4. Deviations from the SOP should be justified, documented, and approved by the CBP QA Coordinator as described in Section II.B.6 below.

5.5. The degree of adherence to the approved SOPs should be determined during systems audits. It is recommended that all SOPs be reviewed at least once a year, revised and approved by his/her supervisor, and submitted for review of changes to the CBP QA and Monitoring Coordinators.

5.6. Laboratory method SOPs should follow a standard format such as the example below.

- 5.6.1. Title Page (method name, number, document control number)
- 5.6.2. Log of Changes to Method
- 5.6.3. Scope and Application (matrices, analytical range, etc.)
- 5.6.4. Definitions
- 5.6.5. Summary
- 5.6.6. Interferences
- 5.6.7. Equipment and Supplies
- 5.6.8. Reagents and Standards
- 5.6.9. Sample Preservation and Storage
- 5.6.10. Quality Control Checks
  - 5.6.10.1. QC samples: Method Blanks, Lab Control Samples, Spikes, Duplicates)
  - 5.6.10.2. Demonstration of capability, etc.)
  - 5.6.10.3.
- 5.6.11. Calibration
- 5.6.12. Analytical Procedure
- 5.6.13. Calculations and Reporting
- 5.6.14. Method Performance Assessment (acceptance criteria, corrective actions, etc.)
- 5.6.15. References
- 5.6.16. Tables, Diagrams, etc.

6. Demonstrating Equivalency of Method Modifications

- 6.1.1.
- 6.1.2. Remaining info in Section F.

7. Procedural Change Authorization

7.1. The CBP Quality Assurance Coordinator must be notified of the intent to make any substantial or long-term change to a procedure or method, either in the field or laboratory.

7.2.

7.3. All modifications should be documented using the Chesapeake Bay Monitoring Program Procedure Modification Tracking Form (PMTF) (Figure II-1). These types of changes include items such as instrument type and sampling stations.

7.4. The completed PMTF should be submitted to the State agency Monitoring Coordinator, CBP Quality Assurance Officer and CBP Database Manager.

7.5. Minor events occurring in the laboratory and detection limit changes must be documented in the CIMS data submission tables.

7.6. At the conclusion of a multiple-day cruise, a Monitoring Cruise Report (Figure II-2) may be completed and submitted to the State agency, who will then forward the information to the CBPO.

Comment [m1]: AMQAW issue

For smaller sampling events, all field information may be reported in the CIMS WQ_Cruise and WQ_Event tables.

7.7. Modifications due to emergencies during a sampling cruise are authorized by the Chief Scientist with priorities for safety and completion of the cruise. Modifications should be reported within 30 days after the cruise. Depending on size or amount of impact on the data the deviation has, the change should be documented in either the PMTF or the Monitoring Cruise Report.

Figure II-1

CHESAPEAKE BAY MONITORING PROGRAM PROCEDURE MODIFICATION TRACKING FORM

PMTF # ________________ ☐ **APPROVED** ☐ **DENIED**

This form is used to request approval for modifications and to document approved modifications made to Chesapeake Bay Program Office procedures or methods. It is not a substitute for timely contact with the CBPO Quality Assurance Officer or his/her designee, who may be reached at 1-800-968-7229. A detailed method description including the proposed modification must be attached to this form prior to submittal to CBPO.

DATE SUBMITTED		DATE APPROVED	
REQUESTOR NAME		ORGANIZATION	
NEWLY PROPOSED [ ] MODIFICATION	FIELD-APPROVED [ ] MODIFICATION	APPROVED BY: DATE:	
TYPE OF PROCEDURE / METHOD	SAMPLING [ ] FIELD [ ] MEASUREMENT	ANALYTICAL [ ] OTHER [ ] SPECIFY:	REPORTING [ ]
DURATION	PERMANENT [ ] TEMPORARY [ ]	EFFECTIVE DATE: START DATE: END DATE:	
PROCEDURE/METHOD DESCRIPTION			
MODIFICATION DESCRIPTION			
JUSTIFICATION FOR MODIFICATION			
ANALYTICAL PARAMETERS THAT MAY BE AFFECTED BY THIS CHANGE			
AFFECTED QA PLAN(S) (TITLE, REVISION, & DATE)			
AFFECTED CRUISE(S)			
PMTF COMPLETED BY	NAME:		DATE:

STATE APPROVAL: NAME ________________________ TITLE ____________

SIGNATURE ________________________ DATE ____________

CBPO APPROVAL: NAME ________________________ TITLE ____________

SIGNATURE ________________________ DATE ____________

8. Sample Handling and Custody

8.1. Procedures should be established that ensure that samples are properly collected, preserved, transported, stored and analyzed within the required holding times.

8.2. The laboratory must establish and operate a system for assuring positive identification of samples and documentation of all samples. To ensure sample integrity, procedures for sample identification, sample receiving, and custody should be developed, instituted and documented.

8.3. Sample Identification

8.3.1. To assure traceability of samples while in possession, there should be a specified method for maintaining identification of samples in the field and throughout the laboratory.

8.3.2. Each sample and sample preparation container should be labeled with a unique identifier that is cross-referenced with the corresponding documentation.

8.4. Sample receiving, storage and disposal requirements are described in Chapter VI, Sections C.2 & C.3.

9. Document Control

Comment [m2]: Deleted information moved to Chapter VI.

9.1. The goal of the document control program is to assure that all documents and electronically stored information from a specified cruise are accountable, secure, and completely retrievable. Document control is recommended for each activity to include electronic as well as hardcopy documentation. Accountable documents should include but not be limited to field and laboratory logbooks, chain-of-custody records, sample work sheets, bench sheets, and other documents relating to the sample or sample analyses. The following document control procedures have been established to assure that all field and laboratory records are assembled and stored for delivery to the CBPO or are available upon request from the CBPO prior to the delivery schedule.

9.2. Preprinted Forms and Logbooks

9.2.1. All documents produced which are directly related to the sampling, preparation, and analysis of CBPO samples should be maintained for inspection by the CBPO. All observations and results recorded by field and laboratory staff but not on preprinted forms should be entered into permanent logbooks. When all data from a cruise are compiled, all original field and laboratory forms and copies of all cruise-related logbook entries should be included in the documentation package.

9.2.2. Pre-printed field and laboratory forms should contain the name of the field crew/laboratory and be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

9.2.3. Logbook entries should be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

9.2.4. Logbook entries should be in chronological order.

9.2.5. Pages in both bound and unbound logbooks should be sequentially numbered.

9.2.6. Data sheets or logs should be maintained to enable a reconstruction of the sample collection or analysis in question.

9.2.7. Corrections to supporting documents and raw data should be made by drawing a single line through the error and entering the correct information. Corrections and additions to supporting documents and raw data should be dated and initialed. No information should be obliterated or rendered unreadable. All notations should be recorded in ink. Unused portions of documents shall be crossed out.

9.3. Storage of Files

9.3.1. Field and laboratory documents will be maintained in a secure location for a period of five years from the date of sample delivery.

10. Consistency of Documentation

10.1. A document control officer responsible for the organization and assembly of the data package should be assigned.

10.2. All copies of field and laboratory documents should be complete and legible.

10.3. Before releasing test results, the document control officer should assemble and cross-check the information on sample tags, custody records, laboratory bench sheets, personnel and instrument logs, and other relevant data to ensure that data pertaining to each particular sample or sample delivery group is consistent throughout the data submittal package.

10.4. All documents relevant to each cruise, including logbook pages, bench sheets, screening records, re-preparation records, records of failed or attempted tests, and custody records should be inventoried.

11. Contingency and Health and Safety Plans

11.1. The Participant should develop and implement the following additional plans:

11.2. A contingency plan covering the availability and/or plan for a backup vessel.

11.3. A contingency plan for key field instrumentation failure.

11.4. A Health and Safety Plan in accordance with all applicable State and Federal regulations.

SECTION C

DATA QUALITY OBJECTIVES

1. Data Quality Objectives

1.1 Data Quality Objectives (DQOs) are qualitative and quantitative statements that specify the quality of data required supporting specific CBPO decisions. DQOs specify the level of uncertainty that a decision maker is willing to accept in results derived from monitoring data. The level of uncertainty is largely a function of sampling frequency and spatial density. DQOs for the Chesapeake Bay Tidal Monitoring Program were established by comparing the power and robustness of various fixed station sampling designs. (Alden et al. 1994).

1.1.1 It was determined that 14 monitoring events, or "cruises", were sufficient for calculating long-term annual trends with acceptable confidence. As funding permits, additional cruises are added to capture major climatic and biological events.

1.1.2 Approximately 100 mid-channel sampling locations or "stations" represent the different regions of the estuary and were selected to represent the Chesapeake Bay segmentation/ characterization scheme, which is based on circulation patterns, salinity, and geomorphology such as tidal fresh, oligohaline, and mesohaline.

2 Measurement Quality Objectives

2.1 Measurement performance criteria for sampling and analytical methods are expressed in terms of Measurement Quality Objectives (MQOs). MQOs are the acceptance thresholds or goals for the data, and are based on the individual data quality indicators (DQIs) for each analyte. The principal indicators of data quality are precision, bias, accuracy, representativeness, comparability, completeness, and sensitivity.

2.2 The DQIs defined in this Section were developed by the CBPO using performance information derived from the CBP laboratories using the methods contained in this document. DQIs are established through an iterative process, these values may be adjusted by the CBP QAO as a result of evaluations of performance data generated during this program.

2.3 Indicators of quality for *sampling* activities are expressed in terms of comparability, representativeness, precision, accuracy, and completeness using the following criteria.

2.3.1 Following the sampling procedures and sample locations recommended in this document may ensure sampling comparability and representativeness of data generated to meet the CBP needs.

2.3.2 Overall precision (sampling and analytical) is assessed through replicate grab or composite samples and may be expressed as relative percent differecnce (RPD). In-situ measurements are not replicated. Sampling precision can be estimated by comparing overall precision to the analytical precision.

2.3.3 Bias from contamination is checked through the analysis of field blanks. Overall accuracy may be assessed through field spike analyses, however, field spike analyses are not recommended for CBP nutrient monitoring.

2.3.4 Sampling completeness is calculated based on the ratio of samples collected to samples that were planned, and is expressed as percent completeness.

2.4 Indicators of quality for in-situ measurements are expressed in terms of comparability, representativeness, completeness, and minimum reporting levels using the criteria listed in Table II.2.

2.4.1 Field measurement comparability and representativeness of data generated are ensured through adherence to the CBP methodologies and quality assurance protocols.

2.4.2 Completeness of measurement data is calculated based on the ratio of measurements made to measurements planned, and is expressed as percent completeness.

2.4.3 Reporting levels for field instruments are based on ____________________

2.5 Indicators of quality for analytical data are expressed in terms of comparability, representativeness, precision, accuracy, completeness, and method detection limits (MDLs), using the following criteria.

2.5.1 Accuracy, expressed as percent recovery, of analytical data is calculated based on the analysis of spiked samples and reference materials.

2.5.2 Completeness of analytical data is calculated based on the ratio of samples that are analyzed to the number of samples collected, and is expressed as percent completeness.

2.5.3 Method detection limits should be determined for all parameters using the procedures recommended by the AMQAW as described below.

2.5.3.1 Samples used in the determination of MDLs should be environmental samples collected once each year during winter, or whenever that analyte's concentration is lowest for the year. The sampling location most appropriate and representative for MDL analyses should be determined before collection.

2.5.3.2 MDL values should be determined as the Student-t (3.14) times the standard deviation of (seven) replicate measurements/analyses of the same sample. Each replicate is processed individually, e.g., filtered, digested, etc.

2.5.3.3 MDLs should be verified for laboratory parameters on an annual basis or whenever a change is made in the measurement or analytical methodology.

2.5.3.4 A table of MDLs values and all supporting documentation should be maintained by the Participant and made available for review as requested by a CBPO representative. When values change, the revised table of MDL values should be included with each data submittal.

2.6 Real-time quality control charts for precision and accuracy should be developed and maintained for each parameter and appropriate concentration ranges, using the most recent 12 months of data. More points may be used if deemed necessary.

2.6.1 Control charts are centered at the arithmetic mean. Unless otherwise specified in the method, the upper and lower control limits are defined at $\pm$ 3 standard deviations from the mean and the upper and lower warning limits are defined at $\pm$ 2 standard deviations from the mean.

2.6.2 Typical precision and accuracy acceptance windows for are provided within each method and in Sections 2, 3, and 4 below.

2.6.3 Once control charts have been established, they should be used to determine if a given analytical or measurement process is in control.

2.6.3.1 A process is out of control if 3 or more data points are outside either control limit.

2.6.3.2 Immediate corrective action is necessary for any process identified as being out of normal control limits. Where possible, this should include reanalysis.

2.6.3.3 A warning of possible systematic error is indicated if 7 successive data points fall away from the mean on the same side of the center line, if 7 or more data points fall outside of either warning limit, or if a discernible trend develops.

3. Data Quality Indicators for Field-Processed Samples

3.1 Objectives for field-processed sample precision, bias and completeness are provided in Table II.1.

Table II.1 Objectives for Field-Filtered Sample Data Quality Indicators

PARAMETERS	REFERENCE	OVERALL PRECISION (FS1 & FS2) or (S1 & S2)	BIAS (Field Blanks)	COMPLETE-NESS
Tidal Water Quality	IV.A.4	Particulate: < 20% RPD		95%
		Dissolved: < 15% RPD		
Nontidal Water Quality	V.C.4	Particulate: < 20% RPD		90%
		Dissolved: < 15% RPD		

4. Data Quality Indicators for Field Measurements

4.1 Post-calibration tolerance, completeness, precision and minimum reporting limit data quality objectives for field measurements are provided in Table II.2.

Table II.2 Objectives for Field Measurement Quality Indicators

PARAMETER	METHOD REFERENCE	POST-CALIBRATION TOLERANCE	COMPLETE-NESS	PRECISION / REPORTING LIMIT
pH	IV.B.3	± 0.2 units	95%	0.1 pH unit
Dissolved Oxygen	IV.B.3	0.3 mg DO/L	95%	0.1– 0.2 mg DO/L
Secchi Depth	IV.B.5	NA	95%	0.1 meter
Specific Conductance	IV.B.3	± 5% of std.	95%	1 umho/cm
Salinity	IV.B.3	NA	95%	0.1 psu
Light Attenuation	IV.B.6	NA	95%	0.05% @ 100% light
Water Temperature	IV.B.3	NA	95%	0.1°C
Depth	IV.B.1.3	NA	95%	0.5 meter

5. Data Quality Indicators for Laboratory Analyses

5.1 Precision, bias, and MDL objectives for laboratory water quality analyses are provided in Table II.3.

5.2 Laboratory precision objectives are based on laboratory replicates, e.g., sample types LS1 & LS2. (Overall precision control limits are based on field-processed replicates, e.g., sample types FS1 and FS2.)

Table II.3. Laboratory Data Quality Indicators for Tidal and Nontidal Water Quality Parameters

PARAMETER	REFER - ENCE	LAB PRECISION (LS1 & LS2)	METHOD BLANK	ACCURACY	Tidal MDL|PQL (mg/L)		Nontidal MDL|PQL (mg/L)
Total Dissolved Phosphorus	IV.D.2			90 - 110 % Spike Recovery	0.001		
Dissolved Ortho Phosphate	IV.D.3			90 - 110 % Spike Recovery	0.0006		
Particulate Phosphorus (PP & PIP)	IV.D.4			90 - 110 % Spiked extract Recovery	0.0012		
Nitrite	IV.D.5			80 - 120% Spike Recovery	0.0002		
Nitrite + Nitrate	IV.D.6			90 - 110 % Spike Recovery	0.0002		
Ammonia	IV.D.7			80 - 120% Spike Recovery	0.004		
Total Dissolved Nitrogen	IV.D.8			90 - 110 % Spike Recovery	0.026		
Particulate Nitrogen	IV.D.9			80 - 120% SRM Recovery	0.019		
Particulate Carbon	IV.D.10			80 - 120% SRM Recovery	0.097		
Dissolved Organic Carbon	IV.D.11			85 - 115% Spike Recovery	0.50		
Chlorophyll-*a*	IV.D.13			N/A	0.2 ***µg/L***		
Pheophytin	IV.D.13			N/A	0.2 ***µg/L***		
Total Suspended Solids	IV.D.14			N/A	2.0		
Silicates	IV.D.16			90 - 110% Spike Recovery	0.013		

SECTION D

FIELD QUALITY CONTROL

1. Annual Calibration

1.1 An annual calibration is an extensive and thorough calibration using standards or instruments traceable to certified (e.g. National Institute of Standards and Technologies) instruments or standards. Annual calibrations of *in-situ* instruments may be performed by a manufacturer or specialized service contractor.

1.2 Annual calibrations will be performed on each field instrument, with the exception of LiCor® meters, where calibration is recommended annually, and required every two years.

2. Routine Calibration

2.1 Field staff shall calibrate *in-situ* instruments before and after each sampling event, deployment, or multiple-day cruise to ensure that the field instrument response is comparable to the response that existed at the annual calibration.

2.2 Instrument calibrations are performed according to manufacturers' specifications.

2.2.1 Routine calibration is required for *in-situ* dissolved oxygen (DO), pH, and conductivity measurements (but not for depth, PAR and temperature).

2.2.2 For dissolved oxygen, a calibration check is recommended at the beginning of each sampling day. If daily DO checks deviate by $\geq$ 0.30 mg DO/L from the expected value, the sensor must be recalibrated before using. If a calibration check (daily or post-calibration) is $\geq$ 0.50 mg DO/L, censor all data corresponding back to the last calibration check using the CIMS WQ Problem Code "V" (Sample results rejected due to QC criteria).

2.2.3 Calibration of Dataflow and extended *in-situ* deployments are performed for DO, pH, conductivity, chlorophyll and turbidity measurements. (See Participants QAPP for most approved procedures.)

2.3 SOPs for calibration should describe the preparation and use of the standard reference solution(s). If commercially prepared standards are used, cite the commercial source(s) in the field SOP and mark the date received on the bottle or calibration log.

2.4 When the calibration check indicates that a significant change occurred during a cruise, the instrument should be serviced and re-calibrated as described in the annual calibration.

2.5 If a daily or post-calibration check does not meet tolerances, qualify all data corresponding to the last calibration performed. (Problem code???)

3. Calibration Samples

Calibration samples are water samples or independent *in-situ* measurements used to develop a statistical relationship between an *in-situ* measurement and the parameter of concern. One example is the collection of grab chlorophyll *a* samples for converting *in-situ* fluorescence measurements into chlorophyll *a* estimates. A second example is the collection of PAR measurements for converting *in-situ* turbidity measurements into corresponding light attenuation coefficients (Kd).

4. Data Quality Objectives for Field Measurements

Data quality objectives for field measurement post-calibration tolerance, completeness, precision and minimum reporting limit are provided in Table II.2.

Table II.2 Field Measurement Quality Objectives

PARAMETER	METHOD REFERENCE	POST-CALIBRATION TOLERANCE	COMPLETE-NESS	PRECISION / REPORTING LIMIT
pH	IV.B.3	± 0.2 units	95%	0.1 pH unit
Dissolved Oxygen	IV.B.3	0.3 mg DO/L	95%	0.1– 0.2 mg DO/L
Secchi Depth	IV.B.5	NA	95%	0.1 meter
Specific Conductance	IV.B.3	± 5% of std.	95%	1 umho/cm
Salinity	IV.B.3	NA	95%	0.1 psu
Light Attenuation	IV.B.6	NA	95%	0.05% @ 100% light
Water Temperature	IV.B.3	NA	95%	0.1°C
Depth	IV.B.1.3	NA	95%	0.5 meter

5. Field Replicate Samples

5.1. Field Split (FS1 & FS2): Two representative portions are taken from one homogeneous sample and processed identically. The data from the field split samples are an indicator of reproducibility (precision) in the sample preparation and analysis steps.

5.2. Field Duplicate, Co-located (S1 & S2): A field duplicate is a sample taken at the same sample location and depth as a CBP sample. The duplicate and sample shall be taken in quick succession of each other. The data from field duplicates may be used to estimate overall precision or to deduce sampling precision.

5.3. The recommended frequency for collecting Field Split or Field Duplicate samples is according to the CBP monitoring program:

5.3.1. Mainstem Monitoring: Collect a field split or a field duplicate once for every 20 samples.

5.3.2. Tidal Tributary Monitoring: Each sampling group should collect field splits once per month, from both surface and bottom depths.

5.3.3. Non-tidal Monitoring: At least one field split sample per month or once for every 20 samples. Field split samples are collected from the churn splitter.

6. Field Blanks

6.1. A field blank is an equivalent aliquot of reagent water that is carried through the entire analytical procedure. The purpose of a field blank is to determine the levels of contamination associated with the processing and analysis of samples.

Blank values are NOT to be subtracted from sample results.

6.2. Field-filtered blanks are required for CBP monitoring programs that specify field filtration. **After** routine samples are processed, filter and preserve reagent grade water exactly the same as the samples. Both dissolved and particulate fractions shall be processed and submitted for analysis.

6.3. The frequency for preparing field-filtered blanks is according to the CBP monitoring program:

6.3.1. Mainstem Monitoring: Prepare one field-filtered blank each day.

6.3.2. Tidal Tributary Monitoring: Prepare at least one field-filtered blank per month.

6.3.3. Non-tidal Monitoring: Prepare at least one field-filtered blank per month. Fill a churn splitter with reagent water prior to filtration.

6.4. If the concentration of a field blank exceeds the PQL, or the lowest analytical standard in the calibration curve, field and/or laboratory contamination should be suspected and corrective action initiated. Corrective action includes an investigation of possible contamination sources (e.g., instrument calibration check, field blank water, sample containers, etc.) and procedural modifications if necessary.

7. Sampling Equipment Blanks

7.1. Equipment blanks indicate the effectiveness of the sampling equipment cleaning procedure. The equipment blank may be processed in the office laboratory after the equipment has been cleaned.

7.2. An equipment blank is required once per year or whenever new equipment is used for the first time.

7.3. The equipment blanks consist of reagent grade deionized water that has been passed sequentially through each component of the sample processing and collection equipment, e.g., submersible pump and hose, Rosette bottles, sampling containers, churn splitter, filtration unit, etc.

7.4. An analysis of the unfiltered reagent grade water used to prepare the blanks maybe helpful in interpreting the results if contamination is found.

7.5. If the concentration of the equipment blank exceeds the lowest analytical standard in the calibration curve, prepare blanks of just the sampling equipment to isolate the cause of the contamination.

8. Decontamination

Table II-D. Summary of Field QC Sample Requirements

Field QC Sample	Frequency	Control Limit
Field Rep (FS1/FS2)	Mainstem: 1 rep. per 20 samples Tidal Tributary: 1 station per month, at all depths Non-tidal: ≥ 1 per month (FS1/FS2)	10 - 30% RPD, Parameter specific
Field Filtration Blank	Mainstem: Daily Tidal Tributary: 1 station per month, at all depths, by each region or sampling team. Non-tidal: ≥ 1 per month	< Lowest analytical standard (PQL)
Field Equipment Blank	Annually	< Lowest analytical standard (PQL)

SECTION E

EXTERNAL PERFORMANCE ASSESSMENTS

1. Split Sample Programs – Interlaboratory Comparisons

1.0 Background and Objectives

All laboratories participating in Chesapeake Bay Water Quality monitoring programs are required to participate in the Chesapeake Bay Coordinated Split Sample Program (CSSP). The CSSP was established in June 1989 by recommendation of AMQAW, to the Monitoring Subcommittee. The major objective of this program is to establish a measure of data comparability among Participants in the monitoring programs.

There are two CSSP sample types; the first is a saline water matrix, collected from the mainstem of the Bay. The second is a fresh water tributary sample, collected from the Potomac River. CSSP samples are collected four times a year for each type, and transported to the laboratories for processing the following morning.

1.1 Summary of Criteria

1.1.1 The Participant will participate in the applicable component(s) of the CSSP.

1.1.2 The SOPs that are developed and used should be in accordance with the Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines, Revision 4 (December 2010) plus any revisions specified by the CBP QAO.

1.1.3 For each of the CSSP stations and on a quarterly basis, the Participant will receive and analyze three or four sub-samples. Treating each sub-sample as a discrete sample, participating laboratories are generally required to perform only those analyses which they routinely perform in support of basin-wide data collection programs. One of the three sub-samples should be used to generate laboratory duplicates and a laboratory spike. These QC samples should be analyzed concurrently with the associated CSSP sub-samples.

1.1.4 The routine submission of split sample data is the responsibility of each laboratory and its in-house data management organization.

1.1.5 To supplement the analyses of the CSSP sub-samples and the respective QC sample, a certified standard reference material (SRM) for each parameter should be analyzed where available. The analysis of standard reference materials provides a strong measure of comparability between all laboratories and within one laboratory's analytical system over time. It is a critical element of any diagnostic efforts associated with the CSSP.

2. Performance Testing

2.1 The University of Maryland Chesapeake Biological Laboratory prepares blind audit samples for all water quality parameters. The blind audit samples are distributed semi-annually to participating laboratories.

2.2 Laboratories also participate in the USGS Standard Reference Sample study for nutrients. Lab managers are advised to analyze both high and low concentrations unless one concentration far exceeds their normal ranges of operation.

3. Audits of Data Quality

3.1 State agency staff will review field blank and field duplicate data to assess the quality of sampling activities.

Comment [m3]: Does this occur in each program? We plan on automating this in the new QAT.

3.2 Analytical and measurement data should be reviewed in order to assess the quality of measurement and analytical activities, respectively.

3.3 The CBP-provided software will electronically verify the data quality for every submittal or the data review criteria will be implemented.

3.4 The Participant will prepare and submit a summary with each data set. The summary must include an explanation for each data point that did not meet the QC criteria established for each method, and deviations that occurred during the generation of the data.

3.5 The Participant will be informed if any of the submitted data do not fall within the prescribed QC limits. Any errors found will be corrected by the Participant at no additional cost to the CBPO.

3.6 The CBP Grant Project Officer has the ultimate responsibility to accept or reject each data submittal.

4. On-Site Audits

4.1 The CBP QAO or representative will conduct periodic on-site evaluations of field and laboratory activities. The frequency of these on-site audits may be increased depending on the Participant's performance. On-site evaluations are carried out to monitor their ability to collect and analyze samples according to the DQOs established by the CBP Monitoring Program.

4.2 The CBP QA Coordinator and a State representative will inspect the Participant's field and laboratory facilities to verify the adequacy and maintenance of instrumentation, the continuity of personnel meeting experience and/or education requirements, and the acceptable performance of analytical and QC procedures. The Participant should expect that items to be monitored will include but not be limited to the following:

- Size and appearance of the facility.
- Quantity, condition, availability, and scheduled maintenance and performance of instrumentation.

- Availability, appropriateness, and use of field and laboratory SOPs.
- Field and laboratory staff qualifications, experience, and personnel training programs.
- Reagents and sample storage facilities.
- Reagent and test solutions preparation logbooks and raw data.
- Field and laboratory bench sheet and logbook maintenance and review.
- Review of the sample analysis/data package inspection procedures.

4.3 Prior to an on-site evaluation, various documents pertaining to performance of the Participant is integrated in a profile package for discussion during the evaluation. Items that may be included are previous on-site reports, laboratory evaluation sample scores, review of data, QA materials, and data trend reports.

4.4 The CBP QAO or representative will discuss his/her findings with the Participant in the presence of a representative from the State agency. During the debriefing, the auditor will present his/her findings and recommendations for corrective actions to field and laboratory personnel.

4.5 Following an on-site evaluation, audit reports which discuss deficiencies found during the on-site evaluation will be forwarded to the Participant. The Participant must respond to the audit report within 30 days of the report and, concurrently, the report must be sent to the CBP QAO and the State representative.

4.5.1 If the Participant fails to take appropriate corrective action to resolve the deficiencies discussed in the on-site reports, any further sampling or analytical activities will not be conducted.

SECTION F
COMPARABILITY STUDIES

1. Background

Chesapeake Bay Program (CBP) data are used to calculate long-term trends in contaminants, which require very precise, unbiased data that are comparable over long periods of time. Seemingly insignificant changes in procedures may cause step-trends over time. To prevent this, the CBP requires that the effects of any change in instruments, reagents, calibration, digestion procedures, etc., be quantified, documented and submitted to the CBP QA Coordinator prior to implementing.

The spirit of allowing a method modification is that the change results in improved method performance measures such as accuracy, a lower detection limits, or better precision. This guidance may be used to evaluate the comparability of a new instrument to be used for the same method.

2. Demonstrating Equivalency of Method Modifications

2.1. Although EPA allows certain changes in methods without official approval under 40 CFR Part 136. 6, ***the Chesapeake Bay Program requires that documentation be submitted to and approved by the CBP QA Officer prior to implementation.*** Analysts should consult the full text of §136.6 before undertaking method modifications to ensure EPA requirements are satisfied.

2.2. Changes will be allowed if the modified method produces equivalent QC performance for the analyte(s) of interest, and the equivalent performance is documented.

2.3. When validating new procedures, laboratories must adhere to the standardized QC detailed in the CBP method and incorporate these criteria into the method.

2.4. Laboratories must use a reference matrix (usually, reagent water) and field samples for the validation study. If a laboratory intends to apply the method to more than one matrix type, the laboratory must validate the method on field samples of each matrix type. Fresh water and saline waters are considered different matrices.

2.5. The new method must meet or exceed the performance measures of the original method. These measures include MDL, spike, duplicate and blank results; calibration checks, standard reference material, calibration correlation coefficients, etc.

2.6. Modifications to procedures for method-defined analytes such as TSS and chlorophyll, or a change that would result in measurement of a different form or species of an analyte are not allowed.

2.7. Modifications that require only CBP approval include:

2.7.1. Changes between automated and manual discrete instrumentation.

2.7.2. Changes between automated and manual sample preparations such as digestions, distillations, and extractions (provided that the temperatures and/or exposure times are maintain same as manual method to achieve same performance).

2.7.3. Changes in the calibration range (provided that the modified range covers any relevant regulatory limit).

2.7.4. Changes in equipment that is similar to equipment from a vendor cited in the method.

2.7.5. Changes in pH adjustment reagents or buffer reagents provided that the changes do not produce interferences.

2.7.6. Changes in equipment operating parameters such as minor changes in the monitoring wavelength of a colorimeter or modifying the temperature program for a specific GC column.

2.7.7. Adjusting sample sizes or changing extraction solvents to optimize method performance in meeting regulatory requirements.

3. Validation of Method Modifications

3.1. Method Compilation

Prior to conducting a validation study, the laboratory should document (or reference) the exact procedures that will be used for the new method. The new method should be followed as written. If changes are necessary during the course of validation, then the date and rationale for the changes should be noted. All measures of performance must be repeated following a change in procedure.

3.2. Method Detection Limit Study

The lab must use the procedures specified in the modified method to perform a method detection limit (MDL) study in accordance with the procedure given at 40 CFR Part 136, Appendix B. Each laboratory must perform its MDL study on an instrument that is calibrated to encompass the projected PQL.

3.3. Calibration

Following completion of the MDL study, re-calibrate the instrument to include the PQL concentration. The laboratory must demonstrate that the linearity criterion and the MDL of the modified method are as good as, or better than those of the original method.

3.4. Initial Precision and Recovery

3.4.1. After successfully calibrating the instrument, perform an initial precision and recovery (IPR) analyses using the procedures specified in the EPA reference method. The IPR consists of analyses of four replicates of reagent water spiked with the analytes of interest.

3.4.2. For each analyte, the precision of analysis of the replicates, as determined by the standard deviation or relative standard deviation (RSD) of the measurements, should be less than the standard deviation or RSD specified in quality control (QC) acceptance criteria in the method.

Similarly, for each analyte, the average percent recovery of the measurements should fall within the range of percent recovery specified in the method. If either the precision or recovery test is failed, the test is repeated until the laboratory is able to meet precision and recovery requirements.

3.4.3. Include a minimum of one blank in the initial demonstration, and the concentration of the analyte(s) in the blank should be less than the level(s) specified in the method. Repeat the initial demonstration with the modified method as an integral part of the method, until the QC acceptance criteria in the method for precision and recovery and for the blank are met. Otherwise, the modification will not be permitted. Maintain records that document that the initial demonstration was performed on the modified method and those requirements for precision and recovery and the blank were met.

3.5. Field Sample Validation

After successful completion of IPR analyses, the method modification is to be validated on the matrix type(s) chosen for the validation study. The numbers of analyses should be 100 samples per matrix, and cover the typical ranges of seasonal, concentration and spatial differences.

3.6. Ongoing Precision and Recovery

The laboratory must demonstrate that it can meet the precision and recovery QC acceptance criteria of the original method. Each batch of samples which includes field samples, but not the IPR samples, must include an OPR sample.

3.7. Calibration Verification

The laboratory must verify calibration as described in the method. The field samples discussed in Section 3.5 above must be analyzed in a separate batch of determinations from the initial calibration sequence, so that calibration verification is performed. Calibration verification sample results of the modified method must meet the acceptance criteria of the original method. Ideally, 30 calibration verification sample pairs would provide more confidence in the statistical analysis. Recommend at least 5 CCV samples of several (3 to 5) different concentrations.

3.8. Contamination Level in Blanks

The laboratory must prepare and analyze at least one method blank with each sample batch during which the matrix samples are prepared and analyzed. The actual number of blank samples analyzed by each laboratory must meet or exceed the frequency specified in the method. The laboratory modified method must demonstrate that it can meet the QC acceptance criterion for blanks that is specified in the method.

4. Statistical Analysis

4.1. A *paired t-test* is best for the comparison of two different methods on samples of different concentrations, especially if the differences between pairs are normally distributed. A two-sided test with a p-value of 0.01 is recommended.

4.2. A *Wilcoxin Signed-Rank test* is necessary when the differences between the sample pairs are not normally distributed.

4.3. An *Analysis of Variance* (SAS® PROC GLM, a General Linear Model) is recommended if one wants to compare the effects of interferences on the different methods. Samples with the potential to interfere must be identified to conduct this analysis.

Note: A regression analysis that compares one method directly against another is NOT recommended since neither method can be assumed to have no error. Such an analysis would result in a "regression dilution effect". However, some labs have used linear regression when the paired t-test showed a significant difference and a correction factor was needed for an unavoidable method change.

5. Documentation

5.1. See Table II.4

Table II.4 Documentation of Method Equivalency

	New Method	Current Method	EPA Method
1. Title and Description *List & attach SOPs for new and current.*			
2. Procedural differences			
3. Concentrations of calibration standards			
4. Initial Precision & Recovery			
5. Calibration Verification *-Initial Cal Verification Result* *-Ongoing Cal Verification Res*			
6. Method Detection Limit			
7. Correlation coefficient of calibration curve			
8. Sample matrix and concentration range for each *(fresh and saline waters are separate matrices)*			
9. Paired t-test results *(per each matrix) A two-sided t-test with p-value of 0.01*			
10. Wilcoxin Signed-Rank test *(if paired differences are not normally distributed)*			
11. Other Statistics			
12. Certified reference material results *with certified values*			
13. PT sample and results *(USGS, ERA, CBP blind audit, etc.)*			
14. Method blank results			
15. Instrument blank *(if comparing instruments)*			
16. Spiked sample results *(Sample conc. and % recovery of each spike)*			
17. Duplicate sample results *(Rep 1, Rep 2 values and RPDs)*			
19. Raw Data sample pairs *(Submit Excel file or equivalent)*			

20. Analyte carry-over			

SECTION H

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APPENDIX II-A

QA PROJECT PLANS and LABORATORY QUALITY MANUAL

1. Quality Assurance Project Plan

The QA Project Plan shall be composed of standard elements that cover the entire project from planning, through implementation, to assessment. The document *EPA Requirements for QA Project Plans (QA/R-5)* fully describes the necessary elements which are summarized below.

A. Project Management

The elements in this group address the basic area of project management, including the project history and objectives, roles and responsibilities of the participants. These elements ensure that the project has a defined goal, that the participants understand the goal and the approach to be used, and that the planning outputs have been documented.

B. Data Generation and Acquisition

The elements in this group address all aspects of project design and implementation. Implementation of these elements ensure that appropriate methods for sampling, measurement and analysis, data collection or generation, data handling, and QC activities are employed and are properly documented.

C. Assessment and Oversight

The elements in this group address the activities for assessing the effectiveness of the implementation of the project and associated QA and QC activities. The purpose of assessment is to ensure that the QA Project Plan is implemented as prescribed.

D. Data Validation and Usability

The elements in this group address the QA activities which occur after the data collection phase of the project is completed. Implementation of these elements ensures that the data conform to the specified criteria, thus achieving the project objectives.

A1 Title and Approval Sheet
A2 Table of Contents
A3 Distribution List
A4 Project/Task Organization
A5 Problem Definition/Background
A6 Project/Task Description
A7 Quality Objectives and Criteria
A8 Special Training/Certification
A9 Documents and Records

B1 Sampling Design (Experimental Design)
B2 Sampling Methods
B3 Sample Handling and Custody
B4 Analytical Methods
B5 Quality Control
B6 Equipment Testing & Maintenance
B7 Instrument & Equipment Calibration
B8 Inspection & Acceptance of Supplies
B9 Non-direct Measurements
B10 Data Management

C1 Assessments & Response Actions, i.e., corrective action
C2 Reports to Management

D1 Data Review, Verification & Validation
D2 Verification & Validation Methods
D3 Reconciliation with User Requirements

2. **Laboratory Quality Manual** – Suggested Format

1.0 Quality Assurance Policies

1.1 Quality Assurance Policy Statement
1.2 Proficiency Test Program
1.3 Review of Requests for the Acceptance of New Work
1.4 Document Control System (for bench sheets, log books, SOPs, etc.)

2.0 Organization and Responsibilities

2.1 Organizational Chart
2.2 Management
2.3 Laboratory Director, Associate Laboratory Director
2.4 Technical Staff (Include IT, Analysts, etc.)
2.5 Information Management System
2.6 Training
2.7 Laboratory Capabilities

3.0 Quality Assurance Indicators

3.1 Determining Control Limits for:
- Precision & Accuracy
- Representativeness
- Completeness
- Comparability

3.2 Procedure for Method Detection Limit Studies

4.0 Sample Handling

4.1 Sample Tracking
4.2 Sample Acceptance Policy
4.3 Sample Receipt Protocols
4.4 Sample Storage Conditions
4.5 Chain of Custody
4.6 Sample Disposal

5.0 Calibration Procedures and Frequency

5.1 Traceability of Calibration
5.2 Instrument Calibration (initial and continuing)

6.0 Test Methods and Standard Operating Procedures

6.1 Reference Method (authoritative source)